Sci. Bull. (2015) 60(13):1220–1221
DOI 10.1007/s11434-015-0822-z

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Research Highlight

Chemistry

The mechanism behind the DOM effects on methylmercury photodegradation

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Methyl mercury (CH_3Hg^+), a neurotoxin, is the most toxic form of mercury that occurs in natural waters [1–4]. It is a cause of concern because of increasing worldwide pollution by mercury in both water and atmosphere [3, 5]. Photodegradation of CH_3Hg^+ is one of the main removal pathways from surface waters, and it has been shown to occur in the presence of dissolved organic matter (DOM) but not in ultra-pure water [2, 4]. Several mechanisms for the photodegradation of CH_3Hg^+ have been proposed, including: (1) direct photodegradation of CH_3Hg–DOM complexes via intramolecular electron transfer [4] and (2) indirect photodegradation of CH_3Hg–DOM by free radicals/reactive oxygen species such as singlet oxygen ($^1O_2$) and the hydroxyl radical ($HO^\bullet$) [1, 2, 6]. Studies show that the photo-Fenton reaction or the reactive oxygen species, including hydroxyl radical ($HO^\bullet$), $^1O_2$, triplet excited state of DOM ($^3DOM^*$), and hydrated electron (e^-_{aq}), play a minor role in CH_3Hg^+ photodegradation in aqueous media [3, 4, 6]. Interestingly, the photodegradation of CH_3Hg^+ depends on the wavelength-specific incident photon flux, on DOM contents and salinity, but does not depend on nitrate photolysis [3]. It has been shown that rates of CH_3Hg^+ photodegradation are decreased with increasing salinity and DOM contents [3]. Increasing DOM contents with the CH_3Hg^+ aqueous media can act as a barrier to reach the incident light intensity toward the CH_3Hg^+ component which could presumably decline the rates of CH_3Hg^+ photodegradation. Several gaps still exist concerning the proposed photodegradation pathways, including two unresolved key questions: (1) how does DOM form bonds with CH_3Hg^+? and (2) How is the newly formed complex excited upon irradiation? A couple of considerations may help in shedding some light over this issue and could provide scope for further research in the field.

The first issue is the formation of π-electron bonding systems between CH_3Hg^+ [$Hg^{1+} = 1s^22s^22p^63s^23p^6 4s^23d^{10}4p^65s^24d^{10}5p^66s^14f^{14}5d^{10}$] and DOM ($CH_3Hg$–DOM), through electron donation from the functional groups of high molecular weight DOM to an empty *s*-orbital of CH_3Hg^+ (ligand-to-metal charge transfer) [7]. Note that the π-electron bonding system is not formed with low-molecular-weight DOM, because the formed complex would not be stable enough. The overall conditional complexation constants (K'_{DOM}) between Hg(II) and DOM (extracted humic acids, fulvic acids and hydrophobic acids) show very strong interactions ($K'_{DOM} = 10^{23.2\pm1.0}$ L/kg) at Hg/DOM ratios below approximately 1 μg Hg/mg DOM, which are indicative of mercury–thiol bonds [8]. Photodegradation of methylmercury can thus occur via a pathway that involves thiol complexation [2, 4]. In contrast, much weaker interactions ($K'_{DOM} = 10^{10.7\pm1.0}$ L/kg) are observed at Hg/DOM ratios above approximately 10 μg Hg/mg DOM, coherently with Hg binding to oxygen functional groups [8]. The second issue is that π-electrons

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are loosely bound and they are highly susceptible to radiative excitation [7].

The ligand-to-metal charge transfer could be triggered by the photolysis of the complex $H_3C–Hg^+ \leftarrow DOM$ (where the "←" indicates electron donation), which could take place as follows (Eq. (1)):

$$H_3C{-}Hg^+ \leftarrow DOM + h\nu \rightarrow H_3C{-}Hg^{\cdot} + DOM^{+\bullet} \qquad (1)$$

Oxidized DOM ($DOM^{+\bullet}$) could undergo several processes. Interestingly, similar phenomena involving the charge-transfer photolysis of Fe(III)–DOM complexes ultimately cause DOM mineralization via decarboxylation [1]. The species $H_3C–Hg^\bullet$ might, for instance, react with $HO^\bullet$ and/or $^1O_2$ [1, 2]. Oxidizing transients are expected to preferentially react with the methyl moiety of $H_3C–Hg^\bullet$, because the π-electron bonding system would provide an increased electron density on the methyl group and would lower the excitation energy of the carbon–mercury bond [9]. Such processes would lead to the demethylation of $H_3C–Hg^\bullet$, with the formation of elemental Hg and oxidation of the methyl group (Eq. (2)).

$$H_3C{-}Hg^\bullet + {}^1O_2/HO^\bullet \rightarrow Hg + \text{oxidized}\,CH_3 \qquad (2)$$

Note that the formation of Hg^{2+} from the reaction (Eq. (2)) would not occur, because irradiated Hg cannot release its outer electron from the s-orbital and also because of the high availability of hydrated electrons in waters under the light condition [7, 10].

The occurrence of inorganic compounds can also be important: for instance, increasing salinity can decrease the photodegradation of CH_3Hg^+ by several processes [3], including: (1) the scavenging of $HO^\bullet$ by bromide (the main $HO^\bullet$ scavenger in seawater) [7, 10] and (2) the different speciation of the CH_3Hg^+ cation in seawater compared to freshwater. In seawater, the formation of stable complexes/ion pairs with anions such as Cl^- and Br^- may hinder the formation of the photolabile species $H_3C–Hg^+ \leftarrow DOM$.

Acknowledgments This work was supported by the National Natural Science Foundation of China (41210004, 41130536), the Key Construction Program of the National "985" Project, Tianjin University, China, and University of Torino-EU Accelerating Grants, Project TO_Call2_2012_0047.

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